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US PATENT APPLICATION

STRUCTURES, SYSTEMS AND METHODS FOR JOINING ARTICLES AND MATERIALS AND USES THEREFOR

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STRUCTURES, SYSTEMS AND METHODS FOR JOINING ARTICLES AND
MATERIALS AND USES THEREFOR

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation-in-part of, and claims benefit of U.S.
5 Application No. 10/661,381, filed September 12, 2003 which claims benefit of U.S.
Provisional Application No. 60/463,766 filed April 17, 2003, both entitled
“STRUCTURES, SYSTEMS AND METHODS FOR JOINING ARTICLES AND
MATERIALS AND USES THEREFOR.” These prior applications are hereby
incorporated by reference in their entirety.

10 **FIELD OF THE INVENTION**

[0002] The invention relates primarily to the field of nanotechnology. More
specifically, the invention pertains to nanofibers and nanofiber structures which posses
adherent properties, as well as to the use of such nanofibers and nanofiber comprising
structures in the coupling, grasping, holding, and/or joining together of articles or
15 materials.

BACKGROUND OF THE INVENTION

[0003] Joining together or holding of articles and/or materials has been common
for at least thousands of years. Such joining has typically been achieved through use of
adhesives of various types, e.g., exogenous substances applied between articles or
20 materials to be joined which adhere to both of the articles or materials and, thus, join them.
Today, modern adhesives are an integral part of life. Typical modern adhesives comprise
what are known as contact adhesives. Such contact adhesives are usually based upon
variations of soft sticky polymers of varying viscosity, which conform to surfaces and
adhere through van der Waals forces, thereby joining surfaces/materials.

25 [0004] While such typical adhesives are quite useful, they do have a number of
limitations. For example, the layer of adhesive necessary to join surfaces can be
inconveniently thick (e.g., from hundreds of microns to millimeters, etc.). While that
might be acceptable in some situations, it is quite inappropriate in others. Adhesives can

also often leave messy residues. Additionally, adhesives can leak, spread or volatilize from their area of application into other nearby areas where they are not desired. Such spreading can result not only in unintended joining of materials, but can also result in chemical or physical contamination of such other areas.

5 **[0005]** Furthermore, while a wide range of adhesive compounds exists, the majority of them have a (sometimes limited) range of parameters necessary for their use. For example, some adhesives do not work above a certain ambient temperature (e.g., the polymers become too fluid and the adhesive either loses much of its adherent property or leaks away). Other adhesives do not work below a certain temperature (e.g., the adhesive
10 becomes brittle and cracks). Additionally, many adhesives are toxic and/or cause irritation to body tissues which come into contact with them. Yet other adhesives do not adhere in the presence of water, organic solvents and/or vacuum, etc., while other adhesives require such conditions.

[0006] In addition to exogenous adhesive compounds, other adherents such as
15 “hook and loop” or “touch fasteners” e.g., Velcro®, have more recently been used to join materials together. However, such systems also are problematic in typically requiring two groups of specifically shaped fiber groups.

[0007] In the context of the above background, research on new adherents and methods of adhesion has been intrigued by examples of adhesion and adherent ability in
20 the natural world. For example, the ability of geckos, spiders and flies to adhere to seemingly shear surfaces has long fascinated researchers. Geckos’ ability to stick to surfaces without the use of an adhesive substance (such as a polymer, etc.) has been under intense scrutiny recently as a model for adhesion.

[0008] A welcome addition to the art would be an adherent material or surface or a
25 method of adhesion which could be modified to fit different environmental conditions and parameters, which would not migrate to unwanted areas, which would not necessarily require two dedicated surfaces, and which would require no external application of resins, carriers, etc. The current invention provides these and other benefits which will be apparent upon examination of the following.

SUMMARY OF THE INVENTION

[0009] In some aspects the current invention comprises a method of increasing an adherence (or adherent) force between two or more surfaces by providing a first surface (which has a plurality of nanofibers attached to it or associated with it), providing at least a second surface, and contacting the surfaces together (whereby an adherence force between the surfaces is increased in comparison to any adherence force between such surfaces in the absence of the plurality of nanofibers), thereby adhering the surfaces to each other. In some embodiments herein, the surfaces and the plurality of nanofibers can optionally comprise (and be optionally independently selected from) such materials as, e.g., silicon, glass, quartz, plastic, metal, polymers, TiO, ZnO, ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, HgS, HgSe, HgTe, MgS, MgSe, MgTe, CaS, CaSe, CaTe, SrS, SrSe, SrTe, BaS, BaSe, BaTe, GaN, GaP, GaAs, GaSb, InN, InP, InAs, InSb, PbS, PbSe, PbTe, AlS, AlP, AlSb, SiO₁, SiO₂, silicon carbide, silicon nitride, polyacrylonitrile (PAN), polyetherketone, polyimide, an aromatic polymer, or an aliphatic polymer. In optional embodiments herein the nanofibers are non-biological in material or, consist essentially of a non-biological material. In other words, the nanofiber is not, e.g., protein, carbohydrate, lipid, or combinations thereof. The contacting of the surfaces optionally creates van der Waals attraction between the surfaces (e.g., typically greater forces than would exist between such surfaces in the absence of nanofibers). In some embodiments herein such attraction comprises from at least about 0.1 newton per centimeter² to at least about 100 newtons per centimeter², or from at least about 0.5 newton per centimeter² to at least about 50 newtons per centimeter², or from at least about 1 newton per centimeter² to at least about 25 newtons per centimeter², or from at least about 2 newtons per centimeter² to at least about 10 newtons per centimeter². Alternatively and/or additionally, the contact of the surfaces creates friction forces between the surfaces which, in typical embodiments, are greater than friction forces that would result from contact of such surfaces (or similar surfaces) without the nanofibers. Furthermore, the first surface of some such embodiments comprises a surface density of members of the plurality of nanofibers from at least about 0.1 nanofiber per micron² to 1000 or more nanofibers per micron²; or from at least about 1 nanofiber per micron² to 1000 or more nanofibers per micron²; or from at least about 5 nanofibers per micron² to 500 or more nanofibers per micron²; or from at least about 10 nanofibers per micron² to 250 or more nanofibers per micron²; or from at least about 50 nanofibers per micron² to 100 or more nanofibers per micron². Additionally, in other

embodiments, the first surface and the at least second surface are composed of the same material.

[0010] Furthermore, in yet other embodiments, the nanofibers are composed of the same material as one or more of the first or second substrates. Other embodiments include where the nanofibers are hollow nanotubular structures. In some embodiments, one or more of the nanofibers comprises one or more associated moiety. In yet other embodiments substantially all nanofibers comprise one or more associated moiety (optionally a coating composed of the one or more associated moiety) which can be a functional moiety in some embodiments. In some such embodiments such functional moiety can increase van der Waals attraction between the nanofiber and the at least second surface (e.g., so that the attraction between the nanofiber and the second surface is greater than the van der Waals attraction between the nanofiber and the at least second surface in the absence of the moiety) or can increase friction forces between the nanofiber and the at least second surface (e.g., so that when a normal force is applied, the friction between the nanofiber and the second surface is greater than the friction between the nanofiber and the at least second surface in the absence of the moiety). The functional moiety can include or comprise a covalent bond (e.g., create a covalent bond) between the nanofiber and the at least second surface. In yet other embodiments, not only does the first surface optionally comprise a plurality of nanofibers, but the at least second surface can comprise a plurality of nanofibers attached thereto also. Also in some embodiments, the nanofibers comprise curled or curved nanofibers (or compliant nanofibers that can optionally curve or bend) that touch one or more surface at more than one point and/or which touch one or more surface by contacting the surface with the side of the nanofiber instead of, or in addition to, the tip of the nanofiber.

[0011] In yet other embodiments, such first surfaces can comprise the surface of one or more medical device and such second surfaces can comprise one or more biological tissue (e.g., tissue, such as a vessel, an organ, bone, flesh, plant material, etc., from an biological organism). Such biological tissue can be within an organism (i.e., *in vivo* or *in planta*) or can be outside of an organism (i.e., *ex vivo*, *in vitro*, or *ex planta*). Furthermore, such biological tissue can comprise an entire organ (e.g., a whole liver) or can comprise part(s) of an organ (e.g., a biopsy sample or a lobe from a liver). Also, the surface (i.e., comprising the nanofibers) can optionally touch just a small area of the biological tissue

(e.g., as when a probe or retractor touches an internal organ) or can touch large percentages or even the entirety of the biological tissue (e.g., when a laminar patch comprising adherent nanofibers is placed upon an organ or vessel, etc.). Biological tissue can optionally come from any living, or previously living, organism (e.g., animal, plant, amphibian, reptile, bird, mammal, primates, nonhuman primates, humans, etc.).

Nonlimiting examples of such devices optionally comprise, e.g., clamps (e.g., c-clamps, barrel clamps, circular clamps, etc.), stents, shunts, probes, retractors, patches and/or bandages, laminar sheets, medical meshes, etc. In typical embodiments, the surface(s) of the device which adhere to the biological tissue comprise nanofiber surfaces. Thus, for example, in embodiments comprising stents, the adherent nanofiber surface is typically the surface that comes into contact with the biological tissue, e.g., a blood vessel, a meatus, a duct, etc. For example, a stent going inside a blood vessel would typically comprise adherent nanofiber surfaces on the outside portion of the stent that would come into contact with the inside of the vessel.

[0012] In other aspects, the invention comprises a method of joining two or more articles. Such method comprises providing a first article (with at least a first surface comprising a plurality of nanofibers attached to it or associated with it), providing at least a second article having at least a first surface, and mating the first surface of the second article with the plurality of nanofibers on the first surface of the first article (so that the nanofibers contact the first surface of the second article at a plurality of contact points) whereby forces between the nanofibers and the first surface of the second article adhere the first article to the second article (i.e., more than adherence that might occur in the absence of the nanofibers). In optional embodiments herein the nanofibers are non-biological in material or, consist essentially of a non-biological material. In other words, the nanofiber is not, e.g., protein, carbohydrate, lipid, or combinations thereof. In some typical embodiments such adherent forces comprise van der Waals forces. In other typical embodiments, such forces can alternatively or additionally comprise friction forces (e.g., as when a normal force is applied). Such embodiments optionally comprise a density of contact points per unit area (i.e., the contact density or intimate contact area, etc.) of the second surface. The density of contact points can optionally comprise contact of from at least about 1 nanofiber per micron² to 2000 or more nanofibers per micron²; or from at least about 5 nanofibers per micron² to 1000 or more nanofibers per micron²; or from at least about 10 nanofibers per micron² to 500 or more nanofibers per micron²; or from at

least about 50 nanofibers per micron² to 250 or more nanofibers per micron²; or from at least about 75 nanofibers per micron² to 150 or more nanofibers per micron². Of course, in some embodiments, e.g., when nanofibers curve and touch a surface more than once, the measurements are typically nanofiber contacts per square micron of the surface. In some embodiments the plurality of contact points (i.e., the contact density or intimate contact area, etc.) comprises a percent contact area of the second surface, which can optionally comprise from about 0.1% to at least about 50% or more; or from about 0.5% to at least about 40% or more; or from about 1% to at least about 30% or more; or from about 2% to at least about 20% or more; or from about 5% to at least about 10% or more of the area of the second surface. Furthermore, embodiments herein can optionally comprise a plurality of contact points comprising a density of contact points per unit area of the second surface and comprising a percent contact area of the second surface. Thus, the density of contact points can comprise contact of from at least about 1 nanofiber per micron² to about 2000 or more nanofibers per micron², from at least about 5 nanofibers per micron² to about 1000 or more nanofibers per micron², from at least about 10 nanofibers per micron² to about 500 or more nanofibers per micron², from at least about 50 nanofibers per micron² to about 250 or more nanofibers per micron², or from at least about 75 nanofibers per micron² to about 150 or more nanofibers per micron², and can also comprise a percent contact area of the second surface from about 0.1% to at least about 50% or more, from about 0.5% to at least about 40% or more, from about 1% to at least about 30% or more, from about 2% to at least about 20% or more, or from about 5% to at least about 10% or more.

[0013] In other aspects, the present invention comprises a method of joining two or more articles, by providing a first article having at least a first surface, providing at least a second article having at least a first surface; and providing a layer of nanofibers disposed between the first surface of the first article and the first surface of the at least second article, whereby the nanofibers contact the first surface of the first article and the first surface of the at least second article at a plurality of contact points, so that forces between the nanofibers and the first surface of the first article and the first surface of the at least second article adhere the articles together (i.e., wherein such forces between the articles (e.g., via the nanofibers) are greater than forces between the articles in the absence of the nanofibers). In typical embodiments such forces comprise van der Waals forces and/or friction forces (e.g., as when a normal force is applied to the surfaces). In such

embodiments, the nanofibers are optionally non-biological in material or, consist essentially of a non-biological material. In other words, the nanofiber is not, e.g., protein, carbohydrate, lipid, or combinations thereof.

[0014] In such typical methods of joining two or more articles herein such first
5 articles can comprise a surface of one or more medical device and such second surfaces can comprise one or more biological tissue (e.g., tissue (such as a vessel, an organ, bone, flesh, plant material, etc.) from an biological organism). Such biological tissue can be within an organism (i.e., *in vivo* or *in planta*) or can be outside of an organism (i.e., *ex vivo*, *in vitro*, or *ex planta*). Furthermore, such biological tissue can comprise an entire
10 organ (e.g., a whole liver) or can comprise part(s) of an organ (e.g., a biopsy sample or a lobe form a liver). Also, the surface (i.e., comprising the nanofibers) can optionally touch just a small area of the biological tissue (e.g., as when a probe or retractor touches an internal organ) or can touch large percentages or even the entirety of the biological tissue (e.g., when a laminar patch comprising adherent nanofibers is placed upon an organ or
15 vessel, etc.). Biological tissue can optionally come from any living, or previously living, organism (e.g., animal, plant, amphibian, reptile, bird, mammal, primates, nonhuman primates, humans, etc.). Nonlimiting examples of such devices optionally comprise, e.g., clamps (e.g., vasculature clamps, c-clamps, barrel clamps, circular clamps, etc.), stents, shunts, probes, retractors, patches and/or bandages, laminar sheets, medical meshes, etc.
20 In typical embodiments, the surface(s) of the device which adhere to the biological tissue (s)comprise nanofiber surfaces. Thus, for example, in embodiments comprising stents, the adherent nanofiber surface s typically the surface that comes into contact with the biological tissue, e.g., a blood vessel, a meatus, a duct, etc. For example, a stent going inside a blood vessel would typically comprise adherent nanofiber surfaces on the outside
25 portion of the stent that would come into contact with the inside of the vessel.

[0015] In yet other aspects herein, the invention comprises an adherent (or adhering or adhesive) device comprising a first article (having at least a first surface), at least a second article (having at least a first surface) and, a layer of nanofibers disposed between the first surface of the first article and the first surface of the at least second
30 article, whereby the nanofibers contact the first surface of the first article and the first surface of the at least second article at a plurality of contact points, such that forces between the nanofibers and the first surface of the first article and the first surface of the at

least second article adhere the articles together (i.e., wherein such forces between the articles are greater than forces between the articles in the absence of the nanofibers). In some embodiments, one or more of the first article and the at least second articles comprise the nanofibers, while in yet other embodiments, the nanofibers are between the surfaces, but are not part of the surfaces. In optional embodiments, the nanofibers are optionally non-biological in material or, consist essentially of a non-biological material. In other words, the nanofiber is not, e.g., protein, carbohydrate, lipid, or combinations thereof. In typical embodiments the forces comprise van der Waals forces and/or friction forces. Such devices also include wherein one or more of the first surface and the at least second surface comprise a plurality of nanofibers, and also wherein physical contact between the first and at least second substrate produces a van der Waals attraction and/or friction force between the surfaces. In some embodiments, such attraction can comprise from at least about 0.1 newton per centimeter² to at least about 100 newtons per centimeter², from at least about 0.5 newton per centimeter² to at least about 50 newtons per centimeter², from at least about 1 newton per centimeter² to at least about 25 newtons per centimeter², or from at least about 2 newtons per centimeter² to at least about 10 newtons per centimeter². In certain aspects, embodiments can comprise hollow nanotubular structures and the nanofibers can optionally comprise one or more associated moiety (optionally a functional moiety, e.g., one which causes a van der Waals attraction and or a friction force between the nanofiber and one or more of the surfaces to be greater than a van der Waals attraction and/or friction force between the nanofiber and such surface in the absence of the moiety). In some embodiments, the second article can comprise one or more of: a metal, a plastic, a ceramic, a polymer, silicon, quartz, glass, wood, biological tissue, plant tissue, animal tissue, bone, stone, ice, a composite material, etc. Such devices can comprise those for grasping (e.g., grasping the at least second article). For example, the second article can comprise a biological tissue which can be grasped (e.g., controllably adhered) to the first article (e.g., a probe, laminar patch, etc.). Such controllable adherence can optionally be temporary (e.g., for a limited time) or can be essentially permanent, or can last only as long as selected conditions exist (e.g., environmental or milieu conditions around the adherence area). Such devices can also optionally comprise those for positioning two or more articles (e.g., biological tissues). For example two tissues can optionally be positioned relative to one another, e.g., as in wound closure, etc. Such devices can comprise any of a number of medical devices (e.g., screws, nails, staples,

probes (e.g., touch probes), laminar sheets (e.g., bandages, patches, laminar strips, etc.)).

In yet other embodiments, such devices can optionally include wherein the second article also has at least a second surface and wherein the device also has at least a third article

(with at least a first surface) and also wherein a second layer of nanofibers is disposed

5 between the second surface of the second article and the first surface of the third article.

Thus, in such embodiments, the nanofibers also contact the second surface of the second

article at a plurality of contact points and the first surface of the at least third article at a

plurality of contact points so that forces between the nanofibers and the second surface of

the second article and the first surface of the third article adhere the articles together. In

10 typical embodiments, the adherent forces between the articles is greater than an adherent

force between the articles in the absence of nanofibers. Such devices can also optionally

comprise medical devices. For example, the first and third articles (and optionally

additional articles) together can comprise a clamp (e.g., vasculature clamps, c-clamps,

barrel clamps, etc.), a binding staple, a pair of forceps, a vise grip, a circular clamp, a

15 barrel clamp, a medical clip, etc.

[0016] These and other objects and features of the invention will become more fully apparent when the following detailed description is read in conjunction with the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

20 [0017] **FIGURE 1:** Displays a photomicrograph of an exemplary adherent nanofiber structure of the invention.

[0018] **FIGURE 2, Panels A and B:** Schematically illustrate the contact and van der Waals attractions and/or friction forces between nanofibers and/substrate surfaces.

25 [0019] **FIGURE 3, Panels A, B, C and D:** Schematically illustrate various concepts of intimate contact between nanofibers and substrate surfaces.

[0020] **FIGURE 4:** Schematically illustrates construction and design of an exemplary device embodiment of the invention.

DETAILED DESCRIPTION

[0021] As stated previously, contact adhesives are often based on soft, sticky polymers that conform to surfaces and adhere through van der Waals forces.

Unfortunately, common contact adhesives are subject to a number of limitations. For example, the layer of such contact adhesive needed to adhere materials together is usually hundreds of microns to millimeters thick and such adhesives can soften with increased temperature. Such typical contact adhesives can also often leave unwanted residues on surfaces or even outgas over time.

[0022] Typical contact adhesives rely on low modulus polymers having low glass transition temperatures. Such contact adhesives, thus, can conform to surfaces on a nanometer scale and form van der Waals bonds at ambient application temperatures. However, the low modulus of the polymers often leads to poor load bearing capabilities, softening of the adhesive at elevated temperatures, and brittleness at low temperatures. Additionally, typical adhesive compounds or mixtures often include tackifiers (e.g., coumarone/indene resins, phenol/terpine resins, etc.) to increase adhesion. Unfortunately, such tackifiers are often volatile, and therefore reduce the utility of such adhesives in medical applications, aerospace applications, clean room applications and the like

[0023] Other common types of adhesive compounds include, e.g., two-part reactive adhesives (such as epoxies) and solvent-based or heat-activated adhesives. These types of adhesive compounds often require at least a moderate level of skill to apply and can often release vapors until they are cured or set. The vapors released can be hazardous and/or toxic to animal/plant life or can cause decay of nearby materials such as plastics or fibers which come into contact with the vapors. If a structural or covalent bond is desired, these adhesive compounds also often require primers or coupling agents to prepare the surfaces to be bound before the liquid adhesive is applied.

[0024] Another disadvantage to common adhesive compounds is that they experience shrinkage during cure or polymerization. The shrinkage can be, e.g., up to 2-5% on epoxies, etc. Shrinkage can be extremely detrimental in many situations. For example, adhesive shrinkage can cause misalignment of surfaces and even material breakage. Additionally, many common adhesive compounds cannot be used in medical applications or settings because of their toxic/irritative nature and/or because they will not adhere under medical conditions.

[0025] The current invention comprises adherent materials and methods of adhering two or more articles, materials, or surfaces together while avoiding such problems as, e.g., thick adhesive layers, volatility, the performance restrictions of low modulus/low glass transition temperature materials, etc. The adherent materials and methods of the invention are, depending upon grammatical context and the like, also sometimes referred to herein as adhesion materials and methods, or even adhesive materials and methods. However, it will be appreciated that similarity to traditional “contact adhesives” etc. is not implied, nor should be inferred.

[0026] Without being bound to a particular theory or mechanism of operation, the concept of nanofiber adhesion of the invention is believed to operate on the principle that even high modulus materials (e.g., silicon), when present as fine enough nanofibers, will be compliant enough to allow close access between the fibers and a secondary substrate. This closeness activates van der Waals forces between the fibers and the secondary surface and so generates adhesion between the nanofibers and the secondary surface. Of course, if the nanofibers are attached (either covalently or through van der Waals forces, etc.) to a first substrate, then the first and second substrates will be adhered together (e.g., via the nanofibers). In other embodiments, it is believed that friction forces created between the high surface area between the nanofibers and an opposing surface optionally joins the surfaces together (e.g., prevents their movement relative to one another, prevents slipping, etc.), e.g., when normal force is applied. As explained in greater detail below, the nanofibers involved herein allow greater contact between surfaces than would otherwise be the case. This is because the individual fibers are rigid enough to “stand up” from one surface and touch the other surface and compliant enough to bend/give, etc. to touch the various irregularities in the other surface, thus, making greater contact than would otherwise occur. See, discussion of Figure 3 below. This increase in intimate surface area contact (i.e., touching) between the surfaces can therefore lead to increased van der Waals forces and/or increased friction between the surfaces.

[0027] Although the current invention is described generally in terms of adhesion and joining of articles, etc., it will be appreciated that such terms, and, thus, the present invention, encompass more transient associations between surfaces, e.g., providing for enhanced gripping or friction between surfaces, that may be applied to myriad different applications including those specifically described herein. For example, grasping/holding

of objects, prevention of slipping of surfaces past one another (e.g., when a normal force is applied between the objects), etc. are all encompassed within the current invention.

[0028] As stated previously, some recent research in adhesion, *see*, e.g., K. Autumn et al., *Nature* (2000) 405:681-685, has focused on the physical surface structures of gecko feet. The gecko's foot surfaces, which in some aspects are similar to synthetic nanofibers, have been offered as an explanation for the gecko's amazing climbing ability. As shown in the Examples below, this principle (i.e., adhesion through physical surface structure rather than exuded polymers, or other similar contact adhesives, etc.) has been expanded and proven for nanofibers (e.g., crystalline nanofibers, etc.). *See*, below. As explained, the concepts and uses of the current invention are also optionally used with other materials such as carbon nanotubes and metallic nanofibers, etc. and other materials that combine the desired properties of rigidity and compliance. Typically, in some preferred embodiments, the materials comprising the nanofibers are non-biological materials, e.g., are not proteins, carbohydrates, lipids, etc., or combinations thereof.

[0029] The close proximity that the nanofibers achieve to the secondary surface also, in some embodiments, allows covalent bonding when the two surfaces are appropriately functionalized. *See*, below. Such covalent bonding previously has only been done through use of high forces and pressures and between hard surfaces (i.e., to generate the intimate contact needed) or with liquid systems. However, as explained herein, when nanofibers comprised of an appropriately rigid material, which also comprises the appropriate compliance (e.g., crystalline nanofibers) are attached to a first substrate and are contacted with a second substrate, they adhere instantly and form a structural bond. The nanofiber substrates herein can be adhered to a wide variety of secondary substrates including glass, steel and plastic, or more generally, ceramics, metals, polymers, etc., as well as biological tissue, with significant adhesion. Of course, it will be appreciated that the greatly increased surface areas involved in the contact between nanofibers/surface, etc. can also allow for a stronger bond when traditional adhesive substances are applied (e.g., as when a traditional polymer adhesive is used in conjunction with the nanofiber surfaces herein).

[0030] In typical embodiments herein, a layer of nanofibers is provided between two or more surfaces that are to be joined or adhered. The layer of nanofibers form coupling interactions with the surfaces, thus, joining/adhering them together. Providing

the nanofibers between the surfaces is optionally accomplished by providing the fibers covalently coupled to a first surface (e.g., by growing nanofibers directly on the first surface or by, e.g., separately covalently attaching the fibers to the first surface), followed by mating the fiber-covered surface with a surface of a second article or material.

- 5 Additionally and/or alternatively, nanofibers are optionally deposited on one or both surfaces and permitted to associate with the initial surface by the same mechanism which is ultimately exploited to couple the second surface to the first surface (e.g., van der Waals forces, friction forces, or the like). Other embodiments comprise wherein nanofibers are grown on and/or deposited upon one or both sides of a flexible foil, flexible sheet, or the like which is inserted between two or more articles and, thus, forms a bond between the nanofibers on the flexible foil and surfaces of the two or more articles. Other
10 embodiments comprise nanofibers present on both surfaces of articles to be joined. One of skill in the art will readily grasp the various permutations of nanofiber placement/deposition upon various surfaces, interstices, etc. comprised within the invention
15

- [0031] In some embodiments, the invention involves contacting a first surface and at least a second surface, so that van der Waals forces cause the surfaces to adhere together. Of importance in such embodiments herein is that the first surface (and in some embodiments the second surface also) comprises a plurality of nanofibers attached to, or
20 associated with, the surface. The presence of the nanofibers allows a much greater surface area of contact between the two surfaces and the intimate contact thus formed allows van der Waals forces to adhere the surfaces to one another and/or allows increased friction between the surfaces (or keeps the surfaces from sliding past one another, etc.). As explained above, other embodiments herein comprise nanofibers deposited between two
25 surfaces, etc. *See*, above.

- [0032] In typical embodiments herein, the surfaces (i.e., the surfaces to be adhered) and the nanofibers on the surfaces (whether on one surface or on both surfaces, free nanofibers deposited between the surfaces, or on a third surface between the first and second surfaces) can optionally comprise any number of materials. The actual
30 composition of the surfaces and the nanofibers is based upon a number of possible factors. Such factors can include, for example, the intended use of the adhered surfaces, the conditions under which they will be used (e.g., temperature, pH, presence of light (e.g.,

UV), atmosphere, etc.), the amount of force to be exerted on the bond between the surfaces (as well as the direction of such forces, e.g., normal or parallel, etc.), the durability of the surfaces and the bond, whether the surfaces are present in a biological/medical setting, cost, etc. For example, the ductility and breaking strength of nanowires will vary depending on, e.g., their composition. Thus, ceramic ZnO wires can be more brittle than silicon or glass nanowires, while carbon nanotubes may have a higher tensile strength. If the strength of the attachment of a nanowire to a substrate is lower than the van der Waals bonding strength or the friction force when a normal force is applied, such can help determine the strength required to break the adhesion. Again, in typical embodiments, the nanofibers are comprised of non-biological material (e.g., they are not made up of proteins (e.g., keratin, etc.), carbohydrates, lipids, etc., or combinations thereof).

[0033] Some possible materials used to construct the nanofibers and nanofiber surfaces herein, include, e.g., silicon, ZnO, TiO, carbon, carbon nanotubes, glass, and quartz. *See*, below. The nanofibers of the invention are also optionally coated or functionalized, e.g., to enhance or add specific properties. For example, polymers, ceramics or small molecules can optionally be used as coating materials for the nanofibers. The optional coatings can impart characteristics such as water resistance, improved mechanical or electrical properties or higher van der Waals forces and/or friction forces, anti-bacterial activity, etc. In other words, in some embodiments a moiety or coating added to a nanofiber can act to increase the van der Waals attraction between such nanofiber and a substrate/surface it is to be adhered to and/or can increase friction, e.g., when a normal force is applied, between the nanofiber and a substance/surface it is to be adhered to. Additionally, in some embodiments, a moiety or coating can serve as a covalent binding site (or other binding site) between the nanofiber and a substrate/surface it is to be adhered to.

[0034] Of course, it will be appreciated that the current invention is not limited by recitation of particular nanofiber and/or substrate composition, and that any of a number of other materials are optionally used in different embodiments herein. Additionally, the materials used to comprise the nanofibers can optionally be the same as the material used to comprise the first surface and the second surface (or third surface, etc.), or they can be

different from the materials used to construct the first surface or the second surface (or third surface, etc.).

[0035] In various embodiments herein, the nanofibers involved are optionally grown on a first substrate and then subsequently transferred to a second substrate which is used in the adhesion process. Such embodiments are particularly useful in situations wherein the substrate desired needs to be flexible or conforming to a particular three dimensional shape that is not readily subjected to direct application or growth of nanofibers thereon. For example, nanofibers can be grown on such rigid surfaces as, e.g., silicon wafers or other similar substrates. The nanofibers thus grown can then optionally be transferred to a flexible backing such as, e.g., rubber or the like. Again, it will be appreciated, however, that the invention is not necessarily limited to particular nanofiber or substrate compositions. For example, nanofibers are optionally grown on any of a variety of different surfaces, including, e.g., flexible foils such as aluminum or the like. Additionally, for high temperature growth processes, any metal, ceramic or other thermally stable material is optionally used as a substrate on which to grow nanofibers of the invention. Furthermore, low temperature synthesis methods such as solution phase methods can be utilized in conjunction with an even wider variety of substrates on which to grow nanofibers. For example, flexible polymer substrates and other similar substances are optionally used as substrates for nanofiber growth/attachment. See below for a more detailed discussion and references.

[0036] In yet other embodiments herein, the nanofibers involved can optionally comprise physical conformations such as, e.g., nanotubules (e.g., hollow-cored structures), nanowires, nanowhiskers, etc. A variety of nanofibers are optionally used in this invention including carbon nanotubes, metallic nanotubes, metal nanofibers and ceramic nanofibers (again, all preferentially of non-biological composition, see above). As long as the fibers involved are concurrently rigid enough to extend above a primary surface and compliant enough (e.g., capable of molding or conforming or bending to meet or come into contact with an uneven surface, see, discussion of Figure 3 below) to make intimate contact with a secondary surface and have the appropriate chemical functionality (whether arising innately or through addition of a moiety to the nanofiber) to generate strong enough van der Waals forces, friction forces, or other physical or chemical interactions to generate adhesion forces, then such nanofibers are optionally used in the invention. Thus,

those of skill in the art will be familiar with similar nanostructures (e.g., nanowires and the like) which are amenable to use in the methods and devices of the invention.

[0037] In various embodiments herein, van der Waals attraction between a first surface and at least a second surface can optionally comprise greater than about 0.1
5 newton per centimeter² or more (e.g., when measured in relation to the areas of the surfaces). Of course, such van der Waals attractions are typically (but not necessarily solely) between the nanofibers and the second surface and optionally the nanofibers and the first surface.

[0038] Additionally, in other embodiments herein, van der Waals forces between
10 individual nanofibers on a first surface and a second surface can optionally comprise, e.g., from about 1 newton per centimeter² to about 100 newtons per centimeter² or more. In some embodiments van der Waals forces between individual nanofibers on a first surface and a second surface optionally comprise approximately 2 newtons per centimeter². Again, it will be appreciated that recitation of specific force amounts between surfaces and
15 nanofibers, etc. should not be construed as necessarily limiting. This is especially true since the present invention encompasses myriad nanofiber and substrate compositions which can optionally affect the van der Waals and other forces between the nanofibers and/or substrates which, in turn, affect the level of adhesion involved. Furthermore, as explained below, various functionalities (either inherent to the nanofibers and/or substrates
20 or added to the nanofibers and/or substrates) optionally act to alter the van der Waals or other attractive forces between the nanofibers and/or substrates. Thus, recitation of exemplary adherent forces (e.g., 1 newton per square centimeter, etc.) should not be taken as necessarily limiting since the invention encompasses various configurations which present any of a number of different levels of adherence. Typically, however, the level of
25 adherence (e.g., whether measured as by increases in van der Waals forces, friction forces, etc.) is greater between the adherent nanofiber surfaces of the invention than between similar surfaces without nanofibers.

[0039] It is to be understood that this invention is not limited to particular configurations, which can, of course, vary (e.g., different combinations of nanofibers and
30 substrates and optional moieties, etc. which are optionally present in a range of lengths, densities, etc.). It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting. As

used in this specification and the appended claims, the singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a nanofiber” optionally includes a plurality of such nanofibers, and the like. Unless defined otherwise, all scientific and technical terms are understood to have the same meaning as commonly used in the art to which they pertain. For the purpose of the present invention, additional specific terms are defined throughout.

Functionalization

[0040] Some embodiments of the invention comprise nanofiber and nanofiber surfaces in which the fibers include one or more functional moiety (e.g., a chemically reactive group) attached to them. Functionalized nanofibers will bring such reactive moiety into intimate contact with a surface where it can, e.g., chemically interact with that surface, either through van der Waals forces, friction, or by binding covalently with a chemical group on that surface, etc. Thus, such moieties can optionally comprise components which will form (or help form) a covalent bond between the nanofiber and the surface to which it is contacted. However, in other embodiments, the moieties are optionally groups which increase the dielectric constant of the nanofiber, thus, increasing the van der Waals attraction between the nanofiber and the surface to which it is contacted. In other words, in some embodiments the functional moiety acts to increase the van der Waals attraction between the nanofiber and the surface to be greater than what such force would be without the moiety. Conversely, in some embodiments, such moieties can act to decrease the van der Waals attraction between the nanofiber and the surface (e.g., in uses which require a weaker adherence than would otherwise result without the moiety). Also, certain moieties can optionally increase or decrease friction forces between the nanofibers and opposing surfaces, e.g., when a normal force is applied. Furthermore, the moiety attached/associated with the nanofibers can be specific for another moiety on a surface to be contacted (e.g., streptavidin on either the nanofiber or the surface to be contacted/matched up with biotin on the other surface or an epoxy group matched up with an amine group on the other surface, etc.). Those of skill in the art will be familiar with numerous similar pairings which are optionally used herein (e.g., amines and boron complexes, etc.).

[0041] For example, details regarding relevant moiety and other chemistries, as well as methods for construction/use of such, can be found, e.g., in Kirk-Othmer Concise

Encyclopedia of Chemical Technology (1999) Fourth Edition by Grayson et al (ed.) John Wiley & Sons, Inc, New York and in Kirk-Othmer Encyclopedia of Chemical Technology Fourth Edition (1998 and 2000) by Grayson et al (ed.) Wiley Interscience (print edition)/ John Wiley & Sons, Inc. (e-format). Further relevant information can be found in CRC

- 5 Handbook of Chemistry and Physics (2003) 83rd edition by CRC Press. Details on conductive and other coatings, which can also be incorporated onto nanofibers of the invention by plasma methods and the like can be found in H. S. Nalwa (ed.), Handbook of Organic Conductive Molecules and Polymers, John Wiley & Sons 1997. See also, ORGANIC SPECIES THAT FACILITATE CHARGE TRANSFER TO/FROM
- 10 NANOCRYSTALS USSN 60/452,232 filed March 4, 2003 by Whiteford et al. Details regarding organic chemistry, relevant e.g., for coupling of additional moieties to a functionalized surface of nanofibers can be found, e.g., in Greene (1981) Protective Groups in Organic Synthesis, John Wiley and Sons, New York, as well as in Schmidt (1996) Organic Chemistry Mosby, St Louis, MO, and March's Advanced Organic
- 15 Chemistry Reactions, Mechanisms and Structure, Fifth Edition (2000) Smith and March, Wiley Interscience New York ISBN 0-471-58589-0.

[0042] Thus, again as will be appreciated, the substrates involved, the nanofibers involved (e.g., attached to, or deposited upon, the substrates) and the like can be varied. For example, the length, diameter, conformation and density of the fibers can be varied, as

20 can the composition of the fibers and their surface chemistry.

Measurement of Adhesion

[0043] Adhesion between substrates and nanofibers is optionally measured in a number of ways. By way of example, adherent properties may be measured by a determination of the force required to separate two coupled articles or surfaces or the force

25 required to move/slip two joined/adhered surfaces past one another. Systems for performing such measurements include, e.g., Universal Material Test Systems available from, e.g., Instron Corp. (Canton, MA). Those of skill in the art will be familiar with this and other similar means of measurement of adhesion forces (e.g., van der Waals forces, friction forces, etc.).

- 30 [0044] Alternatively, for rough measurements, adhesion can be measured by attaching weight (which applies a separating force) to one article or surface that is joined to another. The weight is applied and held constant, or applied in increasing amount, until

separation occurs. Comparison is then made between that measurement and a set of controls. Thus, for example, shear strength measurement is optionally determined by applying a force parallel to the contacted surfaces. The dimensions of the contacted areas are optionally determined and the amount of force or weight (applied parallel to the contacted surfaces) needed to break apart the contacted areas is measured, thus, allowing calculation of the bond strength between the surfaces. Again, those of skill in the art will be aware of various ways to measure adherent properties, friction properties, etc.

Density and Related Issues

[0045] Without being bound to a particular theory of operation or mechanism of action, it is believed that the amount of intimate contact between two surfaces, e.g., the areas involved in van der Waals interactions, is directly related to the level of adhesion between the two surfaces. Further, as alluded to above, it is believed that nanoscale fiber surfaces provide enhanced levels of intimate contact relative to planar or flat surfaces (i.e., ones without nanofiber structures), by virtue of their ability to make such intimate contact between the surfaces. Such is true despite the presence of surface variations or contamination from dust, dirt or other particulates. It will thus be appreciated that “flat” surfaces (i.e., ones without nanofiber structures, etc.) are not really flat. They have bumps, ridges, etc. which prevent true intimate contact which would create, e.g., van der Waals attractions, etc. See, e.g., Figure 3a which illustrates a hypothetical mating of two “flat” surfaces, 300 and 310. The schematic of the surfaces shows that actual intimate contact (e.g., which would create van der Waals forces) only occurs at a few locations, 320. Figures 2a and 2b show that greater intimate contact occurs between surfaces when nanofibers are used as described herein, e.g., intimate contact occurs at each point, 230 or 270 where a nanofiber touches surface 210 or 250. As will be appreciated, nanofibers, 220, in Figure 2A are depicted as straight vertical nanofibers whose contact with the surfaces occurs at their tips. Figure 2B, however, depicts nanofibers that curve/curl, etc., and which can have multiple contact points with the surfaces and/or contact a surface along the side of the nanofiber, etc. This, thus, illustrates the wide range of nanofiber types and conformations that are encompassed within the current invention. In Figure 2, the nanofibers are covalently bound to a first surface, 200 or 260, (e.g., the nanofibers are grown on such first surface) but such should not be construed as limiting on other embodiments herein. For example, as detailed herein, nanofibers can be grown on a

separate surface and then transferred to the surfaces to be adhered together, can be not covalently bound to either surface, etc.

[0046] Based upon the foregoing, therefore, it is expected that the amount of intimate contact between a first substrate and a second substrate, in terms of the percentage of the overlapped surface area that is involved in such contact (also referred to herein as the “contact density” or, in some contexts, as the “percent contact” or “percent contact area”), will have a primary effect on the strength of adhesion between the two substrates. In the case of a first article that includes a nanofiber surface bound to a second planar surface, such contact density would be measured by the percentage of area of the second substrate surface that is intimately contacted by the nanofibers on the first surface. Figure 3 schematically illustrates the measurement of contact density using two contacting planar surfaces (Figure 3A), two planar surfaces that are not perfectly planar or between which some dust or dirt has been deposited (Figure 3B), and a nanofiber surface and a planar surface (Figure 3C showing a top view and Figure 3D showing a side view). As can be seen in Figure 3A, while two planar surfaces without nanofibers, 300 and 310, may seem to be in close intimate contact, in reality, due to surface irregularities, etc., they are only in intimate contact at a few points, 320. Such few intimate contact points are typically not enough to generate large enough amounts of van der Waals forces, etc., to adhere the surfaces together. The measurement of the intimate contact in 3A, thus, could be viewed as the amount or percent of the surface area of the surface of 300 which is touched by the surface of 310, i.e., just the amount or percent which consists of contact points 320. Figure 3D shows a similar interaction, but with a nanofiber surface of the invention. Figure 3D schematically displays two surfaces, 380 and 390, which are similar to those in Figure 3A (i.e., 300 and 310), except that one surface, 390 comprises nanofibers, 395, as described herein. As can be seen, the nanofibers allow much greater contact between the surfaces and, thus, generation of greater van der Waals forces, etc.

[0047] The amount or percent of intimate contact area, 360, in Figure 3B consists of just that area of contact between 330 and 340. Obstacle 350 prevents other areas of intimate contact from occurring. Of course, it will be appreciated that area 360 can also be similar to 320 in enlarged view of 3A (i.e., only small points of intimate contact within 360). Figure 3C displays an enlarged top view of Figure 2A. The areas of intimate contact between nanofibers 220 and surface 210 are shown as dotted circles 370 (from a

top view). Thus, the amount or percent of intimate contact (i.e., contact density) would comprise the amount of area within circles 370 (and/or percent of surface area 210 occupied by circles 370). Of course, it is to be understood that Figures 2A, 2B, 3C and 3D, etc. are simplified for illustrative purposes and that typical embodiments can have a greater number of nanofibers, the nanofibers can touch surfaces via the sides of the nanofibers, etc. *See*, throughout.

[0048] Also, it will be appreciated that determination of the amount of intimate contact between two substrates that are joined, e.g., by deposit of nanofibers between the surfaces can be viewed from the point of view of either surface. However, if the nanofibers are covalently joined or grown from a first surface, then the point of view of percent contact, etc. is typically viewed as exemplified above. Also, for joining of surfaces that both comprise nanofiber surfaces, the amount of intimate contact can also be viewed from the point of view of either surface. Again, it will be noted that various nanofibers involved can touch one or more surface one or more times (e.g., through curving or the like) and can touch at different angles than just perpendicular (e.g., a nanofiber can have intimate contact with a surface through touching the surface along the side of the nanofiber, thus, presenting a much greater contact area than just the tip). *See*, e.g., Figures 2B and 3D.

[0049] Contact density between a nanofiber surface and another surface (also optionally comprising nanofibers), and, thus, adhesion, will generally be a function of, *inter alia*, a number of structural characteristics of the nanofiber surface, including the density of wires that are grown or deposited upon the surface(s), the thickness of each fiber, and the length and conformation of each fiber. Regardless of the mechanism of action of the adherent surfaces described herein, the foregoing structural characteristics are expected to show enhanced adhesion between surfaces.

[0050] In terms of density, it is clear that by including more nanofibers emanating from a surface, one automatically increases the amount of surface area that is extended from the basic underlying substrate, and would thereby typically increase the intimate contact area with a second surface. As explained in more detail below, the embodiments herein optionally comprise a density of nanofibers on the first (and optionally second) surface of from about 1 to about 1000 or more nanofibers per micrometer² of the substrate surface. Again, here too, it will be appreciated that such density depends upon factors

such as the diameter of the individual nanofibers, etc. *See*, below. The nanowire density influences the percent contact area (or contact density), since a greater number of nanofibers will tend to increase the percent contact area between the surfaces. As explained above, the van der Waals attraction, friction forces, etc. between the adhered surfaces relies in large part upon the numerous nanofibers on at least one of the surfaces and/or between the surfaces. Such density of nanofibers on a first surface can typically correspond in a rough fashion to a density of contact points on a second surface.

However, as explained throughout, nanofibers which curve, etc. and touch a surface (or even more than one surface) multiple times and/or along the side of the nanofiber will act to increase the amount of intimate contact to be greater than just the number of nanofibers per unit area of the first surface. Therefore, the density of the nanofibers herein has a bearing on the adhesion of the surfaces because such density is one factor in the area of contact between the surfaces.

[0051] The percent contact between a nanofiber (or a group of nanofibers) and a second surface comprises, e.g., the percentage of the second surface, in unit area, touched, contacted, or covered by the one or more nanofiber. Thus, if a second surface consisted of 100 square microns and was touched by a nanofiber whose actual touching point consisted of 10 square microns, then the percent contact (i.e., amount of intimate contact) would be 10%. In some embodiments, herein, the invention can comprise methods and devices wherein the percent contact ranges from, e.g., about 0.01% to about 50% or greater; from about 0.1% to about 40% or greater; from about 1% to about 30% or greater; from about 2% to about 20% or greater; from about 3% to about 10% or greater; from about 4% to about 5% or greater. In some embodiments herein, the percent contact (i.e., intimate contact) optionally comprises from approximately 0.1% to approximately 5% or greater. *See*, Figure 3 above.

[0052] Different embodiments of the invention comprise a range of such different densities (e.g., number of nanofibers per unit area of a substrate to which nanofibers are attached or associated). The number of nanofibers per unit area can optionally range from about 1 nanofiber per 10 micron² up to about 200 or more nanofibers per micron²; from about 1 nanofiber per micron² up to about 150 or more nanofibers per micron²; from about 10 nanofibers per micron² up to about 100 or more nanofibers per micron²; or from about 25 nanofibers per micron² up to about 75 or more nanofibers per micron². In yet other

embodiments, the density can optionally range from about 1 to 3 nanofibers per square micron to up to approximately 2,500 or more nanofibers per square micron.

[0053] In terms of individual fiber dimensions, it will be appreciated that by increasing the thickness or diameter of each individual fiber, one will again, automatically increase the area of the fiber that is able to make intimate contact with another surface, whether such contact is with a fiber that is directly orthogonal to the second surface or is parallel or tangential with that other surface. The diameter of nanofibers herein can be controlled through, e.g., choice of compositions and growth conditions of the nanofibers, addition of moieties, coatings or the like, etc. Preferred fiber thicknesses are optionally between from about 5 nanometers up to about 1 micron or more (e.g., 5 microns); from about 10 nanometers to about 750 nanometers or more; from about 25 nanometers to about 500 nanometers or more; from about 50 nanometers to about 250 nanometers or more, or from about 75 nanometers to about 100 nanometers or more. In some embodiments, the nanofibers comprise a diameter of approximately 40 nanometers. Choice of nanofiber thickness can also be influenced by compliance of such nanofibers (e.g., taking into account that nanofiber's composition, etc.). Thus, since some compositions can produce a less compliant nanofiber at greater diameter such changes can optionally influence the choice of nanofiber diameter.

[0054] In the case of parallel or tangential contact between fibers from one surface and a second surface, it will be appreciated that by providing fibers of varying lengths, one can enhance the amount of contact between a fiber, e.g., on an edge, and the second surface, thereby increasing adhesion. Of course, it will also be understood that for some fiber materials, increasing length may yield increasing fragility. Accordingly, preferred fiber lengths will typically be between about 2 microns (e.g., 0.5 microns) up to about 1 millimeter or more; from about 10 microns to about 500 micrometers or more; from about 25 microns to about 250 microns or more; or from about 50 microns to about 100 microns or more. Some embodiments comprise nanofibers of approximately 50 microns in length. Some embodiments herein comprise nanofibers of approximately 40 nanometer in diameter and approximately 50 microns in length.

[0055] Nanofibers herein can present a variety of aspect ratios. *See, below.* Thus, nanofiber diameter can comprise, e.g., from about 5 nanometers up to about 1 micron or more (e.g., 5 microns); from about 10 nanometers to about 750 nanometers or more; from

about 25 nanometers to about 500 nanometers or more; from about 50 nanometers to about 250 nanometers or more, or from about 75 nanometers to about 100 nanometers or more, while the lengths of such nanofibers can comprise, e.g., from about 2 microns (e.g., 0.5 microns) up to about 1 mm or more; from about 10 microns to about 500 micrometers or more; from about 25 microns to about 250 microns or more; or from about 50 microns to about 100 microns or more

[0056] Fibers that are, at least in part, elevated above the first surface are particularly preferred, e.g., where at least a portion of the fibers in the fiber surface are elevated at least 10 nanometers, or even at least 100 nanometers above the first surface, in order to provide enhanced intimate contact between the fibers and an opposing surface.

[0057] Again, without being specifically bound to a particular mechanism, the bonding or adherence between the surfaces or materials in many embodiments of the current invention is believed to be due to the bonding or adherence due to van der Waals forces between nanofibers and the surfaces or materials. Thus, the nanofibers, because of their high modulus and compliance create a greater surface area of intimate contact between the surfaces than would occur without the nanofibers. This, in turn, allows greater van der Waals forces to be generated and so adhere the surfaces together. Also, without being specifically bound to a particular mechanism, the bonding or adherence between the surfaces of materials in some embodiments of the current invention is believed to be due to increased friction forces between nanofibers and the surfaces or materials. Here again, the nanofibers, because of their rigidity and compliance, create a greater surface area of intimate contact between the surfaces than would occur without the nanofibers. This, in turn, allows or creates a greater friction force to be generated between the surfaces and so increases the force required to slide the surfaces past one another.

[0058] As explained throughout, the nanofibers involved herein can optionally be grown on surfaces (e.g., be covalently bound to such) and interact/bind with a second surface through van der Waals, friction or other forces (e.g., covalently binding in situations wherein the nanofibers are functionalized with moieties, etc.). In other situations herein, nanofibers are grown on a first substrate and transferred to, and bound to, a second substrate, e.g., covalently or through van der Waals forces, friction, etc. The second substrate is then adhered to a third substrate through van der Waals forces, friction forces, or the like between the nanofibers on the second substrate and the surface of the

third substrate. In yet other embodiments, nanofibers are deposited upon or between substrates and attach themselves through van der Waals, or other chemical and/or physical means to both of the surfaces, thus, adhering such surfaces together.

[0059] As seen in Figure 1, the nanofibers optionally form a complex three-dimensional structure. Again, it will be appreciated that in other embodiments of the invention, the nanofibers are more uniform in height, conformation, etc. The degree of such complexity depends in part upon, e.g., the length of the nanofibers, the diameter of the nanofibers, the length:diameter aspect ratio of the nanofibers, moieties (if any) attached to the nanofibers, and the growth conditions of the nanofibers, etc. The bending, interlacing, etc. of nanofibers, which help affect the degree of intimate contact with a secondary surface, are optionally manipulated through, e.g., control of the number of nanofibers per unit area as well as through the diameter of the nanofibers, the length and the composition of the nanofibers, etc. Thus, it will be appreciated that the adhesion of the nanofiber substrates herein is optionally controlled through manipulation of these and other parameters.

[0060] It also will be appreciated that nanofibers can, in optional embodiments, curve or curl, etc., thus, presenting increased surface area for contact between the nanofibers and the substrate surfaces involved. The increased intimate contact, due to multiple touchings of a nanofiber with a second surface, increases the van der Waals attractions, friction forces, or other similar forces of adhesion/interaction between the nanofiber and the second substrate. For example, a single curling nanofiber can optionally make intimate contact with a second substrate a number of times. Of course, in some optional embodiments, a nanofiber can even retouch the first surface if it curls/curves from the second surface back to the first surface. Due to possible multiple contact points (or even larger contact points, e.g., when a curved nanofiber presents a larger intimate contact area than just its tip diameter, e.g., if a side length of a nanofiber touches a substrate surface) between a single nanofiber and a second substrate/surface, the intimate contact area from curled/curved nanofibers can be greater in some instances than when the nanofibers tend not to curl or curve (i.e., and therefore typically present a “straight” aspect to the second surface). Therefore, in some, but not all, embodiments herein, the nanofibers of the invention comprise bent, curved, or even curled forms. As can be appreciated, if a single nanofiber snakes or coils over a surface (but is still just a single

fiber per unit area bound to a first surface), the fiber can still provide multiple, intimate contact points, each optionally with a relatively high contact area, with a secondary surface

Nanofibers and nanofiber construction

5 **[0061]** The term “nanofiber” as used herein, refers to a nanostructure typically characterized by at least one physical dimension less than about 1000 nanometers, less than about 500 nanometers, less than about 200 nanometers, less than about 150 nanometers or 100 nanometers, less than about 50 nanometers or 25 nanometers or even less than about 10 nanometers or 5 nanometers. In many cases, the region or characteristic
10 dimension will be along the smallest axis of the structure.

[0062] Nanofibers of this invention typically have one principle axis that is longer than the other two principle axes and, thus, have an aspect ratio greater than one, an aspect ratio of 2 or greater, an aspect ratio greater than about 10, an aspect ratio greater than about 20, or an aspect ratio greater than about 100, 200, or 500. In certain embodiments,
15 nanofibers herein have a substantially uniform diameter. In some embodiments, the diameter shows a variance less than about 20%, less than about 10%, less than about 5%, or less than about 1% over the region of greatest variability and over a linear dimension of at least 5 nanometers, at least 10 nanometers, at least 20 nanometers, or at least 50 nanometers. Typically the diameter is evaluated away from the ends of the nanofiber (*e.g.*
20 over the central 20%, 40%, 50%, or 80% of the nanofiber). In yet other embodiments, the nanofibers herein have a non-uniform diameter (*i.e.*, they vary in diameter along their length). Also in certain embodiments, the nanofibers of this invention are substantially crystalline and/or substantially monocrystalline. The term nanofiber, can optionally include such structures as, *e.g.*, nanowires, nanowiskers, semi-conducting nanofibers and
25 carbon nanotubes or nanotubules and the like. *See*, above. Additionally, in some embodiments herein, nanocrystals or other similar nanostructures can also be used in place of more “typical” nanofibers to produce increased adherence. For example, nanostructures having smaller aspect ratios (*e.g.*, than those described above), such as nanorods, nanotetrapods, and the like are also optionally included within the nanofiber definition
30 herein. Examples of such other optionally included nanostructures can be found, *e.g.*, in published PCT Application No. WO 03/054953 and the references discussed therein, all of which are incorporated herein by reference in their entirety for all purposes.

[0063] The nanofibers of this invention can be substantially homogeneous in material properties, or in certain embodiments can be heterogeneous (e.g. nanofibers heterostructures) and can be fabricated from essentially any convenient material or materials. The nanofibers can comprise “pure” materials, substantially pure materials, 5 doped materials and the like and can include insulators, conductors, and semiconductors. Additionally, while some illustrative nanofibers herein are comprised of silicon, as explained above, they can be optionally comprised of any of a number of different materials. Again, typically the primary constituents comprising the nanofibers herein are not “biological” materials, e.g., they are not biological molecules such as proteins, 10 carbohydrates, lipids, or the like.

[0064] The nanofibers herein are typically comprised of substances which possess the appropriate rigidity (e.g., to raise the nanofibers above the surface of a substrate) and compliance (e.g., to allow close enough interaction with substrate surfaces to form adherent interactions) and produce one or more desired interaction (e.g., van der Waals 15 attraction, friction forces, covalent binding such as through a moiety group, etc.). The composition of nanofibers is quite well known to those of skill in the art. As will be appreciated by such skilled persons, the nanofibers of the invention can, thus, be composed of any of a myriad of possible substances (or combinations thereof). Some embodiments herein comprise nanofibers composed of one or more organic or inorganic 20 compound or material. Any recitation of specific nanofiber compositions herein should not be taken as necessarily limiting.

[0065] The nanofibers of the invention are optionally constructed through any of a number of different methods; a number of which are referenced herein. Those of skill in the art will be familiar with diverse methods of constructing nanofibers capable of use 25 within the methods and devices of the invention. Again, examples listed herein should not be taken as necessarily limiting. Thus, nanofibers constructed through means not specifically described herein, but which comprise adherent nanofibers and which fall within the parameters as set forth herein are still nanofibers of the invention and/or are used in the devices, or with the methods of the invention.

30 [0066] In a general sense, the nanofibers of the current invention often (but not exclusively, *see* above) comprise long thin protuberances (e.g., fibers, nanowires, nanotubules, etc.) grown from a solid, optionally planar, substrate. Of course, in some

embodiments herein, the fibers are detached from the substrate on which they are grown and attached to a second substrate. The second substrate need not be planar and, in fact, can comprise a myriad of three-dimensional conformations, as can the substrate on which the nanofibers were grown. In some embodiments herein, the second substrate is flexible, which, as explained in greater detail below, optionally aids in binding and release of substrates from the nanofibers.

[0067] For example, if nanofibers of the invention were grown on, e.g., a non-flexible substrate (e.g., such as some types of silicon wafers) they could be transferred from such non-flexible substrate to a flexible substrate (e.g., such as rubber or a woven layer material). Again, as will be apparent to those of skill in the art, the nanofibers herein could optionally be grown on a flexible substrate to start with, but different desired parameters may influence such decisions. A variety of methods may be employed in transferring nanofibers from a surface upon which they are fabricated to another surface. For example, nanofibers may be harvested into a liquid suspension, e.g., ethanol, which is then coated onto another surface. The same van der Waals forces, friction forces, etc., exploited for adhesion of two articles via these nanofibers can optionally provide coupling of the fibers to this new surface. Subsequent mating of a surface of a second article then further exploits such forces in joining the two articles. Additionally, nanofibers from a first surface (e.g., ones grown on the first surface or which have been transferred to the first surface) can optionally be “harvested” by applying a sticky coating or material to the nanofibers and then peeling such coating/material away from the first surface. The sticky coating/material is then optionally placed against a second surface to deposit the nanofibers. Examples of sticky coatings/materials which are optionally used for such transfer include, but are not limited to, e.g., tape (e.g., 3M Scotch® tape), magnetic strips, curing adhesives (e.g., epoxies, rubber cement, etc.), etc. Such transfer materials are then optionally removed through various methods depending upon the transfer materials, etc. for example, ablation, washing, de-magnetizing and other procedures can optionally be used to remove transfer materials.

[0068] The actual nanofiber constructions of the invention are optionally complex. For example, Figure 1 is a photomicrograph of a nanofiber construction capable of use in the current invention. As can be seen in Figure 1, the nanofibers form a complex three-dimensional pattern. The interlacing and variable heights, curves, bends, etc. form a

surface which provides many contact points between the substrates for van der Waals, friction, or other chemical/physical forces to act to adhere substrates together. Of course, in other embodiments herein, it should be apparent that the nanofibers need not be as complex as, e.g., those shown in Figure 1. Thus, in some embodiments herein, the nanofibers are “straight” and do not tend to bend, curve, or curl. However, such straight nanofibers are still encompassed within the current invention.

[0069] As will be appreciated, the current invention is not limited by the means of construction of the nanofibers herein. For example, some of the nanofibers herein are composed of silicon. However, again, the use of silicon should not be construed as necessarily limiting. The formation of nanofibers is possible through a number of different approaches that are well known to those of skill in the art, all of which are amenable to the current invention.

[0070] Typical embodiments herein can be used with various (e.g., existing) methods of nanostructure fabrication, as will be known by those skilled in the art, as well as methods mentioned or described herein. For example, the various methods of creating adherent nanofibers can be performed using nanofibers made by the methods mentioned or described herein or via other methods. In other words, a variety of methods for making nanofibers and nanofiber containing structures have been or can be described and can be adapted for use in various of the methods, systems and devices of the invention.

[0071] The nanofibers herein can be fabricated of essentially any convenient material (e.g., a semiconducting material, a ferroelectric material, a metal, etc.) and can comprise essentially a single material or can be heterostructures. For example, the nanofibers can comprise a semiconducting material, for example a material comprising a first element selected from group 2 or from group 12 of the periodic table and a second element selected from group 16 (e.g., ZnS, ZnO, ZnSe, ZnTe, CdS, CdSe, CdTe, HgS, HgSe, HgTe, MgS, MgSe, MgTe, CaS, CaSe, CaTe, SrS, SrSe, SrTe, BaS, BaSe, BaTe, and like materials); a material comprising a first element selected from group 13 and a second element selected from group 15 (e.g., GaN, GaP, GaAs, GaSb, InN, InP, InAs, InSb, and like materials); a material comprising a group 14 element (Ge, Si, and like materials); a material such as PbS, PbSe, PbTe, AlS, AlP, and AlSb; or an alloy or a mixture thereof.

[0072] In some embodiments herein, the nanofibers are optionally comprised of silicon or silicon oxide. It will be understood by one of skill in the art that the term “silicon oxide” as used herein can be understood to refer to silicon at any level of oxidation. Thus, the term silicon oxide can refer to the chemical structure SiO_x , wherein x is between 0 and 2 inclusive. In other embodiments, the nanofibers can comprise, e.g., silicon, glass, quartz, plastic, metal, polymers, TiO , ZnO , ZnS , ZnSe , ZnTe , CdS , CdSe , CdTe , HgS , HgSe , HgTe , MgS , MgSe , MgTe , CaS , CaSe , CaTe , SrS , SrSe , SrTe , BaS , BaSe , BaTe , GaN , GaP , GaAs , GaSb , InN , InP , InAs , InSb , PbS , PbSe , PbTe , AlS , AlP , AlSb , SiO_1 , SiO_2 , silicon carbide, silicon nitride, polyacrylonitrile (PAN), polyetherketone, polyimide, aromatic polymers, or aliphatic polymers.

[0073] It will be appreciated that in some embodiments, the nanofibers can comprise the same material as one or more substrate surface, while in other embodiments, the nanofibers do not comprise the same material as the substrates. Additionally, the substrate surfaces can optionally comprise any one or more of the same materials or types of materials as do the nanofibers (e.g., such as the materials illustrated herein). Of course, as will be noted below, surfaces can optionally comprise substances quite different from the nanofibers in composition, e.g., biological materials such as human tissue, etc. can comprise a surface involved.

[0074] Some, but by no means all, embodiments herein comprise silicon nanofibers. Common methods for making silicon nanofibers (e.g., which can be used with the method/devices herein) include vapor liquid solid growth (VLS), laser ablation (laser catalytic growth) and thermal evaporation. *See*, for example, Morales et al. (1998) “A Laser Ablation Method for the Synthesis of Crystalline Semiconductor Nanowires” *Science* 279, 208-211 (1998). In one example approach, a hybrid pulsed laser ablation/chemical vapor deposition (PLA-CVD) process for the synthesis of semiconductor nanofibers with longitudinally ordered heterostructures is used. *See*, Wu et al. (2002) “Block-by-Block Growth of Single-Crystalline Si/SiGe Superlattice Nanowires,” *Nano Letters* Vol. 0, No. 0.

[0075] In general, several methods of making nanofibers have been described and can be applied in the methods, systems and devices herein. In addition to Morales et al. and Wu et al. (above), *see*, for example, Lieber et al. (2001) “Carbide Nanomaterials” USPN 6,190,634 B1; Lieber et al. (2000) “Nanometer Scale Microscopy Probes” USPN

6,159,742; Lieber et al. (2000) "Method of Producing Metal Oxide Nanorods" USPN 6,036,774; Lieber et al. (1999) "Metal Oxide Nanorods" USPN 5,897,945; Lieber et al. (1999) "Preparation of Carbide Nanorods" USPN 5,997,832; Lieber et al. (1998)

"Covalent Carbon Nitride Material Comprising C₂N and Formation Method" USPN

5 5,840,435; Thess, et al. (1996) "Crystalline Ropes of Metallic Carbon Nanotubes" Science 273, 483-486; Lieber et al. (1993) "Method of Making a Superconducting Fullerene Composition By Reacting a Fullerene with an Alloy Containing Alkali Metal" USPN 5,196,396; and Lieber et al. (1993) "Machining Oxide Thin Films with an Atomic Force Microscope: Pattern and Object Formation on the Nanometer Scale" USPN 5,252,835.

10 Recently, one dimensional semiconductor heterostructure nanocrystals, have been described. *See*, e.g., Bjork et al. (2002) "One-dimensional Steeplechase for Electrons Realized" Nano Letters Vol. 0, No. 0.

[0076] It should be noted that some references herein, while not specific to "traditional" nanofibers, are optionally still applicable to the invention. For example,

15 background issues of construction conditions and the like are applicable between "traditional" nanofibers and other nanostructures (e.g., nanocrystals, nanorods, etc.) which are optionally within the invention.

[0077] In another approach which is optionally used to construct nanofibers of the invention, synthetic procedures to prepare individual nanofibers on surfaces and in bulk
20 are described, for example, by Kong, et al. (1998) "Synthesis of Individual Single-Walled Carbon Nanotubes on Patterned Silicon Wafers," Nature 395, 878-881, and Kong, et al. (1998) "Chemical Vapor Deposition of Methane for Single-Walled Carbon Nanotubes" Chem. Phys. Lett. 292, 567-574.

[0078] In yet another approach, substrates and self assembling monolayer (SAM)
25 forming materials can be used, e.g., along with microcontact printing techniques to make nanofibers, such as those described by Schon, Meng, and Bao, "Self-assembled monolayer organic field-effect transistors," Nature 413:713 (2001); Zhou et al. (1997) "Nanoscale Metal/Self-Assembled Monolayer/Metal Heterostructures," Applied Physics Letters 71:611; and WO 96/29629 (Whitesides, et al., published June 26, 1996).

30 [0079] Synthesis of nanostructures, e.g., nanocrystals, of various composition is described in, e.g., Peng et al. (2000) "Shape control of CdSe nanocrystals" Nature 404:59-61; Punties et al. (2001) "Colloidal nanocrystal shape and size control: The case of cobalt"

5 Science 291:2115-2117; USPN 6,306,736 to Alivisatos et al. (October 23, 2001) entitled
“Process for forming shaped group III-V semiconductor nanocrystals, and product formed
using process”; USPN 6,225,198 to Alivisatos et al. (May 1, 2001) entitled “Process for
forming shaped group II-VI semiconductor nanocrystals, and product formed using
10 process”; USPN 5,505,928 to Alivisatos et al. (April 9, 1996) entitled “Preparation of III-
V semiconductor nanocrystals”; USPN 5,751,018 to Alivisatos et al. (May 12, 1998)
entitled “Semiconductor nanocrystals covalently bound to solid inorganic surfaces using
self-assembled monolayers”; USPN 6,048,616 to Gallagher et al. (April 11, 2000) entitled
“Encapsulated quantum sized doped semiconductor particles and method of manufacturing
15 same”; and USPN 5,990,479 to Weiss et al. (November 23, 1999) entitled “Organo
luminescent semiconductor nanocrystal probes for biological applications and process for
making and using such probes.”

[0080] Growth of nanofibers, such as nanowires, having various aspect ratios,
including nanofibers with controlled diameters which can be utilized herein, is described
15 in, e.g., Gudiksen et al (2000) “Diameter-selective synthesis of semiconductor nanowires”
J. Am. Chem. Soc. 122:8801-8802; Cui et al. (2001) “Diameter-controlled synthesis of
single-crystal silicon nanowires” Appl. Phys. Lett. 78: 2214-2216; Gudiksen et al. (2001)
“Synthetic control of the diameter and length of single crystal semiconductor nanowires”
J. Phys. Chem. B 105:4062-4064; Morales et al. (1998) “A laser ablation method for the
20 synthesis of crystalline semiconductor nanowires” Science 279:208-211; Duan et al.
(2000) “General synthesis of compound semiconductor nanowires” Adv. Mater. 12:298-
302; Cui et al. (2000) “Doping and electrical transport in silicon nanowires” J. Phys.
Chem. B 104:5213-5216; Peng et al. (2000), *supra*; Puntès et al. (2001), *supra*; USPN
6,225,198 to Alivisatos et al., *supra*; USPN 6,036,774 to Lieber et al. (March 14, 2000)
25 entitled “Method of producing metal oxide nanorods”; USPN 5,897,945 to Lieber et al.
(April 27, 1999) entitled “Metal oxide nanorods”; USPN 5,997,832 to Lieber et al.
(December 7, 1999) “Preparation of carbide nanorods”; Urbau et al. (2002) “Synthesis of
single-crystalline perovskite nanowires composed of barium titanate and strontium
titanate” J. Am. Chem. Soc., 124, 1186; Yun et al. (2002) “Ferroelectric Properties of
30 Individual Barium Titanate Nanowires Investigated by Scanned Probe Microscopy” Nano
Letters 2, 447; and published PCT application nos. WO 02/17362, and WO 02/080280.

[0081] Growth of branched nanofibers (e.g., nanotetrapods, tripods, bipods, and branched tetrapods) is described in, e.g., Jun et al. (2001) "Controlled synthesis of multi-armed CdS nanorod architectures using monosurfactant system" J. Am. Chem. Soc. 123:5150-5151; and Manna et al. (2000) "Synthesis of Soluble and Processable Rod-, Arrow-, Teardrop-, and Tetrapod-Shaped CdSe Nanocrystals" J. Am. Chem. Soc. 122:12700-12706. Synthesis of nanoparticles is described in, e.g., USPN 5,690,807 to Clark Jr. et al. (November 25, 1997) entitled "Method for producing semiconductor particles"; USPN 6,136,156 to El-Shall, et al. (October 24, 2000) entitled "Nanoparticles of silicon oxide alloys"; USPN 6,413,489 to Ying et al. (July 2, 2002) entitled "Synthesis of nanometer-sized particles by reverse micelle mediated techniques"; and Liu et al. (2001) "Sol-Gel Synthesis of Free-Standing Ferroelectric Lead Zirconate Titanate Nanoparticles" J. Am. Chem. Soc. 123:4344. Synthesis of nanoparticles is also described in the above citations for growth of nanocrystals, nanowires, and branched nanowires. Alternatively, to produce multibranched nanofibers gold film is optionally deposited onto a nanofiber surface (i.e., one that has already grown nanofibers). When placed in a furnace, fibers perpendicular to the original growth direction can result, thus, generating branches on the original nanofibers. Colloidal metal particles can optionally be used instead of gold film to give greater control of the nucleation and branch formation. The cycle of branching optionally could be repeated multiple times, e.g., with different film thicknesses, different colloid sizes, or different synthesis times, to generate additional branches having varied dimensions. Eventually, the branches between adjacent nanofibers could optionally touch and generate an interconnected network. Sintering is optionally used to improve the binding of the fine branches. Such multibranched nanofibers could allow an even greater increase in surface area than would occur with non-branched nanofiber surfaces.

[0082] Synthesis of core-shell nanofibers, e.g., nanostructure heterostructures, is described in, e.g., Peng et al. (1997) "Epitaxial growth of highly luminescent CdSe/CdS core/shell nanocrystals with photostability and electronic accessibility" J. Am. Chem. Soc. 119:7019-7029; Dabbousi et al. (1997) "(CdSe)ZnS core-shell quantum dots: Synthesis and characterization of a size series of highly luminescent nanocrystallites" J. Phys. Chem. B 101:9463-9475; Manna et al. (2002) "Epitaxial growth and photochemical annealing of graded CdS/ZnS shells on colloidal CdSe nanorods" J. Am. Chem. Soc. 124:7136-7145; and Cao et al. (2000) "Growth and properties of semiconductor core/shell nanocrystals

typically when a normal force is applied). The invention is especially useful (but is not limited to) situations/conditions that are not conducive to use of more conventional adhesives. For example, many common adhesives are not useful under conditions such as high temperature, low temperature, high or low humidity, vacuum, in medical settings, or other similar conditions which can adversely effect the polymer, resin, etc. used as the adhesive. Furthermore, in certain medical uses such as attachment of medical devices *in vivo* or attachment of medical devices such as metal plates, etc. to bone or teeth, the adhesive used must be non-immunogenic, etc. For further examples of uses of nanofiber surfaces, e.g., in medical applications, etc., *see*, e.g., USSN 60/468,390 filed May 6, 2003, USSN 60/468,606 filed May 5, 2003, and USSN 10/792,402 filed March 2, 2004, all three entitled "Nanofiber Surfaces for Use in Enhanced Surface Area Applications"; USSN 60/549,711 filed March 2, 2004 entitled "Medical Device Applications of Nanostructured Surfaces"; USSN 60/541,463, filed February 2, 2004 entitled "Porous Substrates, Articles, Systems and Compositions Comprising Nanofibers and Methods of Their Use and Production"; and USSN 60/466,229, filed April 28, 2003, entitled "Super-hydrophobic Surfaces, Methods of Their Construction and Uses Therefor," all of which are incorporated herein in their entirety for all purposes.

[0086] The adherent nanofibers/structures of the invention and the methods of their use can easily be tailored to avoid the problems concerning ambient conditions and medical concerns (*see*, above) through manipulation of the parameters herein, e.g., choice of nanofiber composition material and the like. Additionally, the nature of the invention inherently avoids many of the previously mentioned typical problems (and others as well) since the adherent properties of the invention do not rely on extraneous polymers and the like which can break down or creep under extreme conditions. Instead, the current invention optionally relies upon the van der Waals attraction and/or friction between the nanofiber structures and surfaces. Therefore temperature fluctuations and the like do not alter the basic adherent bonds of the invention.

[0087] In some embodiments, the invention can be used to construct climbing or hanging equipment. For example, similar to geckos, the adherent nanostructures herein can optionally be attached to equipment (e.g., gloves, handheld pads and the like), to allow easy grip of surfaces such as walls, ceilings, rock faces, etc. The ability of the invention to be incorporated into flexible forms allows the rocking or peeling away of the nanofibers

from the surface to which they are adhered. The rocking/peeling changes the contact angle of individual nanofibers in relation to the surface they are adhered to and, thus, can cause release of the individual fiber. Such release is, of course, quite useful in typical applications, e.g., in climbing, etc. Conversely, when release is not desired, the contact angle of the nanofibers is optionally not changed and so no release occurs. Such release can also optionally occur with devices/methods of the invention which comprise nanofiber surfaces that are not flexible as well. In such cases, release can be achieved by changing the contact angle, etc. of nanofibers. For example, in a clamping device or the like which incorporates nanofiber adhesion aspects of the invention, release can optionally be done by applying greater separating pressure at one contact area which creates a separating force in that area which is greater than the forces adhering the nanofibers/surfaces in that area.

[0088] This could be done by, e.g., a fulcrum/scissoring motion as is commonly used in scissors/hemostats, etc. which have an X or V shaped body or the like. Thus, the remaining adhering nanofibers would then be under greater separating forces because they would be carrying a greater load (i.e., because other nanofibers were no longer in contact with the opposing surface, etc.) and could therefore be separated in a similar manner. Another point optionally involved in release is that the change in contact angle of the nanofibers between the surfaces can go from, e.g., nanofibers which present their sides to a surface (thus, creating greater intimate contact and greater adherent force) to, e.g., nanofibers which present less of their sides or just their tips to a surface (thus, creating a lower amount of intimate contact and a lower amount of adherent force). Also, in some situations involving frictional adherence, a change in applied pressure (e.g., from lateral to perpendicular to a surface) or a removal or reduction of normal force, can optionally cause release of adhered surfaces.

[0089] Yet other possible embodiments of the current invention include “setting” or “fixing” of devices/materials into place. For example, a screw put into a material (e.g., a metal plate) could be made much more stable and less prone to release by incorporating nanofiber adherents of the invention. Such incorporation could optionally be done by having nanofibers on one or more of the screw or the screw-hole which receives the screw. Also, nanofibers could optionally be placed between the screw and the screw-hole, e.g., via a slurry of nanofibers or the like. See, above. Addition of nanofibers to one or more surface, or addition of slurries or dry mixes of nanofibers, etc. could, thus, be similarly

used to adhere any number of materials (e.g., screw, nails, fasteners, interlocking devices/plates, etc.).

[0090] In yet other embodiments, the methods and devices of the invention can be utilized in, e.g., aerospace applications, medical applications, or industrial processing applications where creation of bonds which are strong at an appropriate temperature, which produce little or no outgassing and which have the potential for reuse is desired.

[0091] In yet other types of embodiments, the devices and methods of the invention can optionally be used in applications wherein a normal force is applied to the substrate surfaces involved, in order to produce adherence of the substrates. Thus again, in some contexts herein, “adherence,” “adhesion,” or the like can refer to prevention or inhibition of lateral or shear movement (e.g., slipping, sliding, or the like between surfaces such as would occur between a medical clamp and a tissue, between two tissues, etc.). Such embodiments can optionally differ from previously described embodiments in that they can require application of a normal force in order to, or to help to, adhere the surfaces. However, because of the nanofiber surfaces herein, friction forces, etc. are believed to produce adherence at lower levels of normal force than would be required in the absence of the nanofibers. See examples below. Thus, such applications are especially useful in situations requiring adherence (again, here meaning prevention/inhibition of lateral movement, e.g., slipping, of surfaces), but which also require a delicate or gentle normal force. In other words, devices/methods of the invention can be used to prevent/inhibit slippage, but with application of much less normal force than would otherwise be required with non-nanofiber systems.

[0092] Therefore, devices and methods of the invention are optionally used in construction of clamps, such as those used in medical devices, hemostats or the like. Currently jaw inserts of medical clamps are typically made of rubber or metal. Rubber is usually the less intrusive option because it provides compliance (e.g., yielding or conforming to shapes due to, e.g., force applied). The addition of serrated areas or protrusions are often used to increase localized forces on the tissue being clamped. Such features are especially used for irregular surfaces such as arteries or tissue. However, the pressure applied (i.e., normal force) to effectively close off an artery or hold tissue, etc., while keeping the tissue, etc. within the clamp, can possibly damage the tissue/artery/etc. involved. Thus, it is desirable to minimize the pressure applied, but still produce the

specific result, e.g., holding a tissue, clamping an artery, etc. Optimization (e.g., reduction) of such pressures, etc. can optionally be achieved by incorporation of nanofiber inserts in medical clamps and the like.

[0093] As one nonlimiting example, thin metal sheets (e.g., approximately 10 to

5 150 um and preferably 25-100 um) which are quite flexible and resistant to permanent deformation can be used for construction of nanofiber adhesive surfaces for the clamps.

Additionally such thin metal sheets are ideal growth surfaces for nanofibers due to their high temperature resistance. For example, stainless steel, titanium, nickel, beryllium

copper and nickel would all be candidate materials for construction of various medical

10 devices incorporating aspects of the invention. Such thin films can be etched or stamped into precise and intricate shapes. *See*, Figure 4 which gives schematics for one possible type of medical clamp. It will be appreciated that numerous other clamp designs and

formations (incorporating the concepts of the current invention) are also possible and that

the illustration in Figure 4 should not be taken as limiting. Secondary operations are

15 typically done to bend and form parts of clamps into three-dimensional shapes. For a

clamp insert with nanofiber adherent areas, flat parts can optionally be etched or stamped

and a secondary operation can optionally be performed by bending the strip into a C shape to make it into a channel to slide into the clamp as well as using the C shape to create

spring forces. Such secondary operations can also optionally stamp or create serrations or

20 protrusions on the clamp. Areas that require nanofibers can then optionally be gold plated for growth of nanofibers. Thus, for example in Figure 4, a sheet of thin metal, 400, can be

stamped or etched to produce various subparts, 410, that can be formed into devices such as clamps. Once removed from the metal sheet, the stamped or etched parts, 410 can be

manipulated in various manners, e.g., bent to the proper conformation, 430 (which shows

25 an end view), and nanofibers can be grown or deposited upon the correct face/aspect of the part (e.g., nanofibers can be grown after gold-plating, etc.). The properly manipulated part

(comprising nanofibers) can then be assembled with other device parts, e.g., a clamp

insert, etc., 440, to produce the device. As will be appreciated, however, numerous

methods exist for creation of nanofibers for use herein (*see*, above) not all of which

30 require gold plating, etc. Stamping and bending operations as would be used to create

such devices are usually quite inexpensive and can result in precise high quality parts.

The spring qualities and high temperature resistance of thin metals can optionally enhance the functionality of the friction/van der Waals characteristics of the nanofiber devices.

Again, however, it will be appreciated that the nanofiber adhesive surfaces of the invention with their frictional/van der Waals forces will require less clamping force (i.e., normal force) on tissues, etc, and will subsequently induce less tissue damage. The forces (e.g., friction, etc.) can prevent sliding or slipping of medical devices, such as clamps, off of tissues, arteries, etc. which are typically coated with blood/bodily fluids that can cause slipping of ordinary clamps, etc.

[0094] As will be appreciated by those skilled in the art, the adherent surfaces and methods herein present a wide, and deep, range of applications in many fields. For example, in medical settings the adherent surfaces/methods herein can be part of myriad devices for use in, e.g., surgery, as implantable devices, etc. The example section below gives but a few of the many possibilities, all of which are contained within the current invention. In a general non-limiting sense, nanofiber adherent medical devices can be categorized as comprising, e.g., two-surface devices (one or more of which surfaces comprise nanofibers or between which nanofibers are present) in which the surfaces adhere to one another; two-surface devices (one or more of which surfaces comprise nanofibers or between which nanofibers are present) in which the surfaces sandwich another article, such as a tissue or vessel, etc., between them; and one-surface devices which surfaces comprise nanofibers, or which surfaces have nanofibers between them and the article (e.g., a tissue) they touch. Yet other exemplary illustrations of, e.g., medical devices which can optionally incorporate the adherent nanofiber devices/methods, etc. herein can be found in, e.g., USSN 60/468,390, filed May 6, 2003 and USSN 60/468,606, filed May 5, 2003, both entitled "Nanofiber Surfaces for Use in Enhanced Surface Area Applications," USSN 60/549,711, filed March 2, 2004 entitled "Medical Device Applications of Nanostructured Surfaces," USSN 60/541,463, filed February 2, 2004 entitled "Porous Substrates, Articles, Systems and Compositions Comprising Nanofibers and Methods of Their Use and Production," and USSN 60/466,229, filed April 28, 2003, entitled "Super-hydrophobic Surfaces, Methods of Their Construction and Uses Therefor," all of which are incorporated herein in their entirety for all purposes. Again, however, specific recitation of specific medical devices, etc. should not be taken as limiting, thus, myriad non-recited medical devices, etc. are also within the purview of, and are part of, the current invention.

[0095] Examples of nanofiber surface devices in which the surfaces touch one another could include, but are not limited to, e.g., those in which tissues are separately attached to each surface (through any means) and in which the two surfaces of the device are attached to each other. Additionally, locking clamps and the like (e.g., in which the position of the device is stabilized such as in an open, partially open or closed position) can comprise locking mechanisms comprised of touching nanofiber surface(s). Of course, such embodiments can optionally comprise more than two surfaces as well.

[0096] Examples of nanofiber surface devices which clamp/grasp/hold articles can include, e.g., typical clamp devices (e.g., hemostats, ring-clamps, etc.) which hold/grasp/immobilize tissues, etc. during medical procedures. In such embodiments, the surfaces of the device typically comprise nanofiber surfaces (and/or nanofibers are optionally placed between the device surfaces and the article to be held). In such situations, two (or more) adherent areas are created, e.g., one on each side of the object held, between the surfaces of the device and the sides of the object. Again, such embodiments can optionally comprise more than two surfaces.

[0097] Examples of nanofiber single surface devices can include such adherent devices as patches, laminar bandages, shunts, stents, retractors, touch-probes, etc. In such devices, the device surface typically comprises the nanofiber surface and/or nanofibers are deposited between the surface of the device and the object to be held/grasped, etc., e.g., a tissue or vessel. As will be appreciated, the increased adherent and/or friction forces of the nanofiber-surfaced devices of the current invention provide for better stability of such devices within organisms, e.g., better stability of the devices within body cavities, meatuses, vasculature, etc. Such devices are held in place better through the addition of nanofibers. Such patches or bandages can optionally be used to close wounds, hold internal tissues together, etc. Additionally retractors and touch probes (e.g., wand devices used to gently adhere to surfaces, thus, allowing manipulation of a tissue, etc. without clamping) are also optional devices herein. Yet other devices within this category can optionally include those such as shunts, stents and the like, e.g., used to stabilize lines, etc. within vessels or organs and/or to stabilize catheters, etc. Thus, for example, in embodiments comprising stents, the adherent nanofiber surface is typically the surface that comes into contact with the biological tissue, e.g., a blood vessel, a meatus, a duct, etc. For example, a stent going inside a blood vessel would typically comprise adherent

nanofiber surfaces on the outside portion of the stent that would come into contact with the inside of the vessel.

5 [0098] Again, those of skill in the art will be cognizant of the myriad permutations, specializations, and embodiments of devices of the current invention (e.g., various types of clamps, stents, etc.)

10 [0099] Additionally, it will also be appreciated that such clamps and the like are optionally used in other areas besides medical settings (e.g., clamping of wires or of tubes in mechanical or industrial applications, etc), but which also would benefit from stable more gentle clamping than occurs with traditional means. Those of skill in the art will be aware of numerous other possible uses for such devices. Those of skill in the art will also be aware of many applications where the nanofiber adherent devices can hold slippery and/or hard to grasp objects (e.g., arteries, tissue, wet tubes, etc.) with a gentle grasp as opposed to a harsh clamping (e.g., harsh because of high pressure and/or sharp ridges or points or the like), which is required with other current devices, to overcome slipperiness
15 issues and provide a firm hold.

Kits/Systems

[0100] In some embodiments, the invention provides kits for practice of the methods described herein and which optionally comprise the substrates of the invention. In various embodiments, such kits comprise a container or containers with, e.g., one or
20 more adhesion substrate as described herein, one or more device comprising an adhesion nanofiber substrate, etc. (e.g., a medical device such as a sterile clamp, etc.).

[0101] The kit can also comprise any necessary reagents, devices, apparatus, and materials additionally used to fabricate and/or use an adhesion nanofiber substrate, device or the like.

25 [0102] In addition, the kits can optionally include instructional materials containing directions (i.e., protocols) for the synthesis of adhesion nanofibers and/or adding of moieties to adhesion nanofibers and/or use of adhesion nanofiber structures and/or devices. Such instructions can optionally include, e.g., instructions on proper handling and use, sterilization, etc. of a medical device or the like. Preferred instructional
30 materials give protocols for utilizing the kit contents (e.g., to use the adhesion nanofibers or adhesion nanofiber methods of the invention). Instructional materials can include

written material (e.g., in the form of printed material, material stored on CD, computer diskette, DVD, or the like) as well as access to an internet site which contains the appropriate instructions.

- 5 [0103] In certain embodiments, the instructional materials teach the use of the nanofiber substrates of the invention in the construction of one or more devices (such as, e.g., sealing devices, attachment devices, medical devices, etc.).

EXAMPLES

Example 1: Construction of an adherent nanofiber substrate.

- 10 [0104] Silicon nanofibers of approximately 40 nanometer in diameter and 50 um in length were grown on a four inch silicon wafer through a standard CVD process using gold colloids (*see*, e.g., above). The fiber density was approximately 2 nanofibers per square micron. To test the adhesion ability of the silicon nanofiber wafer, a microscope slide was suspended in a vertical orientation above a lab bench. A 2 centimeter x 1
15 centimeter piece from the above silicon wafer containing the nanofibers was lightly pressed against the glass slide (with the nanofiber surface touching the glass slide). Thus, the top centimeter of the nanofiber wafer was exposed to the glass while the other centimeter was not in contact with the glass. A 200 gram weight was then attached to the free end of the silicon wafer via a binder clip. The weight was allowed to hang freely,
20 thus, exerting a stress of 2 newtons on the nanofiber/glass interface. There was no measurable movement in the nanofiber joint in 10 days.

Example 2: Construction of an adherent nanofiber substrate.

- [0105] Silicon nanofibers of approximately 40 nanometers in diameter and 50 um in length were grown on a 4 inch silicon wafer by the standard CVD process using gold
25 colloids. *See*, e.g., above. The fiber density was approximately 2 nanofibers per square micron. To test the adhesion ability of the silicon nanofiber wafer to itself, two 2 x 1 centimeter pieces were cut from the silicon wafer containing the nanofibers. One centimeter of the fiber surface of each piece was lightly pressed together. One free end of the pressed pieces was clamped in a vice on a ring stand and a 100 gram weight was hung
30 from the opposite end. The weight was allowed to hang freely, thus, exerting a stress of 1

newton on the nanofiber surface/nanofiber surface interface. There was no measurable movement in the nanofiber joints in 10 days.

Example 3: Reuse of adherent nanofiber substrates.

[0106] The nanofiber substrate in Example 1 was pulled away from the glass in a perpendicular direction. It was then pressed against a second suspended piece of glass and through a similar process was shown to again hold 2 newtons of force.

Example 4: Reuse of adherent nanofiber substrates.

[0107] A nanofiber substrate prepared as explained in Example 1 was pressed against a variety of substrates including stainless steel, Formica®, painted metal and Teflon®. The substrate exhibited enough adherent force to support its own weight for all of the materials except Teflon® of which it slipped off.

Example 5: Coefficient of friction of adherent nanofiber substrates.

[0108] A Micro Scratch Tester (Micro Photonics, Torrance, CA) was used to determine the difference in coefficient of friction between a nanofiber surface of the invention and a similar surface without nanofibers. A glass surface (i.e., a borosilicate glass microscope slide) that was chemically similar to silicon dioxide nanowires (i.e., one possible type/construction of nanofibers of the invention) was tested against a nanofiber surface similar to those used in previous example, *supra*. The nanofiber surface had a coefficient of friction of 2.0 while the glass slide (without nanofibers) had a coefficient of friction of 0.08.

Example 6: Friction forces/gripping of adherent nanofiber substrates.

[0109] A 5-inch piece of fresh pig aorta obtained commercially was clamped at each end while immersed in a tank of whole milk. A pair of typical medical clamps (Novare® Medical, Cupertino, CA) was clamped on to the center of the aorta. These clamps, as is typical with many medical clamps, use silicon rubber disposable inserts in the “jaws” of the clamp. Such devices are currently considered to be state of the art for traction/holding of tissues in medical settings. The “clamp force” of the Novare® clamp (i.e., the pressure exerted upon the vessel) was determined by the jaw position of the clamps. In other words, the jaw position (how tightly the jaws were clamped together) determined the clamping force upon the aorta. The handle of the clamps was attached to a

load cell that was programmed to pull the clamps at a set rate normal to the aorta. The maximum force reached before the clamps slipped off of the aorta was thus measured.

[0110] The test was repeated with the Novare® clamps three times. The average force applied to cause slippage of the clamps off of the aorta was 4lbs. The clamp inserts
5 were then changed from the traditional silicon rubber to a nanofiber surface of the invention. The adherent nanofiber surface comprised silicon nanowires grown on a silicon wafer. The nanofibers in such example were of 40 nm average diameter and 30 microns average length and were present at about 5 nanofibers per square micron of substrate surface. The clamp surface area of the nanofiber surface was the same as the surface
10 measured for the rubber inserts. Additionally, the jaw position of the clamps was equivalent in each testing. The average force required to slip the nanowire surface off of the aorta was 7lbs. No major differences were observed in regard to tissue damage on the aorta from the clamping action. Additionally, both hydrophilic and hydrophobic nanofiber surfaces produced similar adherent action upon the vessel.

15 [0111] As another control, the silicon nanowire surfaces were reversed in the clamps so that the back of the wafer (i.e., without nanofibers) was exposed to the aorta. In such example, a force of only 2lbs was required to slip the clamp off of the vessel.

[0112] While the foregoing invention has been described in some detail for
20 purposes of clarity and understanding, it will be clear to one skilled in the art from a reading of this disclosure that various changes in form and detail can be made without departing from the true scope of the invention. For example, all the techniques and apparatus described above can be used in various combinations. All publications, patents, patent applications, or other documents cited in this application are incorporated by
25 reference in their entirety for all purposes to the same extent as if each individual publication, patent, patent application, or other document were individually indicated to be incorporated by reference for all purposes.